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# Sertifikaat

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# IB04/51458 Certificate

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1. South African Provisional Patent Application No. 2003/6316 accompanied by a Provisional Specification was originally filed at the South African Patent Office on **14 August 2003**, in the name of **RAND AFRIKAANS UNIVERSITY** in respect of an invention entitled: "**A METHOD FOR PREPARING A SEMICONDUCTOR FILM OF A GROUP 1-111-V1 QUARTERNARY OR HIGHER ALLOY**".
2. The photocopy attached hereto is a true copy of the provisional specification and drawings filed with South African Patent Application No. 2003/6316.

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**PRETORIA**

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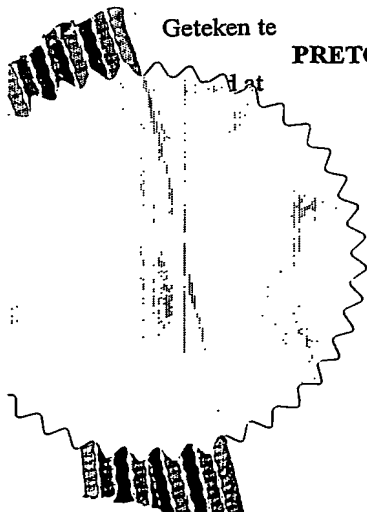
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REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

## REGISTER OF PATENTS

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FULL NAME(S) OF APPLICANT(S) / PATENTEE(S)

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APPLICANTS SUBSTITUTED :

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DATE REGISTERED

ASSIGNEE(S)

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DATE REGISTERED

FULL NAME(S) OF INVENTOR(S)

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PRIORITY CLAIMED

COUNTRY

NUMBER

DATE

N.B. Use international  
abbreviation for country.  
(See Schedule 4)

33

31

32

TITLE OF INVENTION

54 A METHOD FOR PREPARING A SEMICONDUCTOR FILM OF A GROUP I-III-VI QUARTERNARY OR HIGHER ALLOY

ADDRESS OF APPLICANT(S) / PATENTEE(S)

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P27103ZA00

PATENT OF ADDITION NO.

DATE OF ANY CHANGE

61

FRESH APPLICATION BASED ON

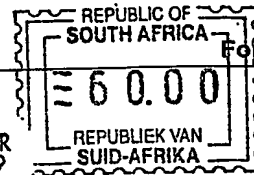
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REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978

APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT  
(Section 30 (1) - Regulation 22)  
The grant of a patent is hereby requested by the undermentioned applicant  
on the basis of the present application filed in duplicate.



P31HR  
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21	01 2003/6316

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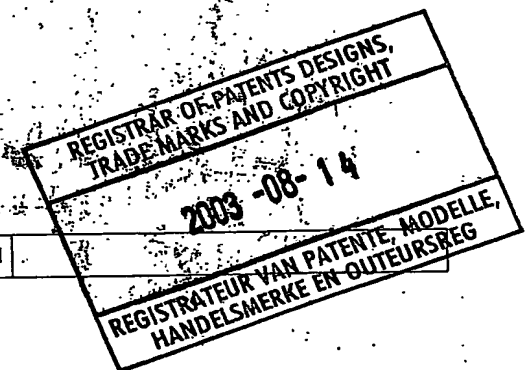
TITLE OF INVENTION
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54	A METHOD FOR PREPARING A SEMICONDUCTOR FILM OF A GROUP I-III-VI QUARTERNARY OR HIGHER ALLOY		
	THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANING FORM P2 The earliest priority claimed is		
	THIS APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO.	21	01
	THIS APPLICATION IS FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON APPLICATION NO.	21	01

THIS APPLICATION IS ACCOMPANIED BY :
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x	1a	A single copy of a provisional specification of 42 pages.
	1b	Two copies of a complete specification of pages.
	2a	Informal drawings of sheets.
x	2b	Formal drawings of 7 sheets.
	3	Publication particulars and abstract (form P8 in duplicate).
	4	A copy of figure of the drawings for the abstract.
	5	Assignment of invention (from the inventors) or other evidence of title.
	6	Certified priority document(s).
	7	Translation of priority document(s).
	8	Assignment of priority rights.
	9	A copy of form P2 and a specification of S.A. Patent Application.
	10	A declaration and power of attorney on form P3.
	11	Request for ante-dating on form P4.
	12	Request for classification on form P9.
	13a	Request for delay of acceptance on form P4.
	13b	

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DATED 14 August 2003

Patent Attorney for Applicant(s)

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## REPUBLIC OF SOUTH AFRICA

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PROVISIONAL SPECIFICATION  
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OFFICIAL APPLICATION NO.		LODGING DATE	DMK REFERENCE
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FULL NAME(S) OF APPLICANT(S)	
71	RAND AFRIKAANS UNIVERSITY

FULL NAME(S) OF INVENTOR(S)	
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TITLE OF INVENTION	
54	A METHOD FOR PREPARING A SEMICONDUCTOR FILM OF A GROUP I-III-VI QUARTERNARY OR HIGHER ALLOY

**A method for preparing a semiconductor film of a group I-III-VI quaternary or higher alloy.**

**Field of the invention**

5

THIS invention relates to a method for the preparation of a semiconductor film, and in particular a group I-III-VI quaternary or higher alloy semiconductor film.

**10 Background to the invention**

For the purposes of this specification the term "pentenary alloy" refers to an alloy having 5 different elements. So for example,  $\text{Cu}(\text{In}, \text{Ga})(\text{S}, \text{Se})_2$  is a pentenary alloy wherein the 5 different  
15 elements are copper (Cu), indium (In), gallium (Ga), selenium (Se) and sulfur (S). Similarly the term "quaternary alloy" refers to an alloy having 4 different elements. Likewise, a ternary alloy has three different elements and a binary alloy has two different elements.

20

Crystalline and multi-crystalline silicon is to date the primary material used in the production of solar modules/photovoltaic cells. The main problem associated with this material is the high cost of manufacturing. In an effort to reduce fabrication costs and  
25 increase material utilization, semiconductor thin film alloys have

been the subject of intensive research. In this regard, group I-III-VI semiconductor films, such as  $\text{CuInSe}_2$  and its alloys with  $\text{CuGaSe}_2$  and  $\text{CuInS}_2$ , are promising candidates for absorber layers in thin film photovoltaic cells or devices.

5

Of particular interest are group I-III-VI semiconductor films comprising Ga in combination with another group III element, since the presence of Ga in such films results in absorber films with higher band gap values and subsequently, in solar/photovoltaic cell devices, with higher open-circuit voltages and reduced short circuit currents. Of even greater interest is pentenary alloy semiconductor films.

In respect of pentenary alloy semiconductor films having  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)(\text{Se}_{1-y}\text{S}_y)_2$  as a general formula, the band gap can be shifted systematically between 1.0 and 2.4eV in order to achieve an optimum match with the solar spectrum. Optimization of this material system has already resulted in laboratory-scale solar cell devices with conversion efficiencies exceeding 18%.

20

Despite the interest in group I-III-VI semiconductor films that comprise Ga, methods of preparing such films have not been perfected. To date, the most successful method for preparing such films are:

25

(a) complex single-stage techniques in which all the elements (Cu, In, Ga, Se and / or S) are co-evaporated from individual sources. This technique allows for the controlled incorporation of gallium and sulfur into the films and hence the formation of homogeneous thin films.

However, the use of this technique has raised many critical questions about its acceptance as a commercially viable process due to large area uniformity problems and poor material utilization. (see M.E Beck, A. Swartzlander, R. Matson et al; Sol. Energy Mater. Sol. Cells; 64, 2000, 135.)

(b) two-step growth techniques, which involve (i) depositing of metallic thin films onto a substrate and (ii) the selenization and/or sulfurization of the metallic thin films in an Se and/or S containing atmosphere. These techniques are disclosed in an article by V. Alberts, J.H. Schön, and E. Bucher, Journal of Appl. Phys. 84(12), 1998, 6881 and by A. Gupta and S. Isomura, Sol. Energy Mater. Sol. Cells 53, 1998, 385.

Whereas the two step growth techniques are capable of commercial application, a number of problems have been encountered such as:

(i) there is poor adhesion of the resultant film to the substrate used to support the semiconductor film;

(ii) there is a reaction between Se and a metallic contact layer provided on the substrate, resulting in the formation of a highly resistive metallic back contact layer.

A further disadvantage with the two-step growth techniques is that the resultant films are heterogeneous. Without wishing to be bound by theory, and solely for the purposes of background, the selenization of thin film metallic precursors such as Cu, In and Ga results in the formation of the binary selenides such as CuSe, InSe and  $Ga_2Se_3$ . Carrying out the selenization reaction under the below prior art conditions results in the binary selenides reacting fully with each other to form discrete, ternary alloys such as  $CuInSe_2$  and  $CuGaSe_2$ , therefore providing a heterogeneous semiconductor film.

Typically, these prior art conditions involve the reactive annealing of the metallic thin film containing Cu, In and Ga in a selenium-containing atmosphere at a single temperature of around 500°C, resulting in:



(a) segregated semiconductor films wherein the semiconductor film comprises two layers of  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$  ternary alloys (where the metallic film is slowly heated over a period of 20 minutes or longer to the reaction temperature, followed by annealing in  $\text{H}_2\text{Se}$  for at least 60 minutes); or

(b) a semiconductor film having a significant degree of inter-diffusion such that the Ga is graded throughout the film, the concentration of Ga increasing from the surface of the film towards the substrate (where the metallic film is heated rapidly within 5 minutes to the reaction temperature, followed by annealing in  $\text{H}_2\text{Se}$  for at least 60 minutes).

The open-circuit voltages ( $V_{oc}$ ) and short circuit currents ( $J_{sc}$ ) of solar modules/photovoltaic cells are directly related to the band gap of the semiconductor material. In the case of  $\text{CuInSe}_2$  with a low band gap value of 1 eV, the  $V_{oc}$  values are typically limited to 500 mV, while values close to 1000 mV can be achieved using a  $\text{CuGaSe}_2$  absorber layer with a higher band gap value of 1.65 eV.

In the case of segregated or graded film structure with most of the gallium residing at the back of the film, the absorber film exhibits a low band gap value in the active region of the photovoltaic cell, which ultimately limits the  $V_{oc}$  of the device. In addition, in the case of graded structures, lattice mismatches

within the graded absorber films introduce electrically active structural defects, which negatively impact on the device performance.

- 5 Once a heterogeneous  $\text{Cu}(\text{In,Ga})\text{Se}_2$  structure is formed, converting the film to a homogeneous material becomes extremely difficult. In an effort to increase the band gap in the near-surface region of the absorber, films are commonly reacted with  $\text{H}_2\text{S}$ .

10

Present industrial processes include a post-sulfurization step in which a certain fraction of the selenium species are replaced with sulfur. (See the articles by K. Kushiya, M. Tachiyuki, T. Kase, I. Sugiyama, Y. Nagoya, D. Okumura, M. Satoh, O. Yamase, and H. Takeshita, *Sol. Energy Mater. Sol. Cells* **49**, 1997, 277; and R. Gay, M. Dietrich, C. Fredric, C. Jensen, K. Knapp, D. Tarrant and D. Willett, *Proceedings of the International Conference on E.C. Photovoltaic Solar Energy*, Vol. **12(1)**, 1994, 935.).

15

- 20 The above approach is hampered by the slow exchange process between the selenium and sulfur in these films, and it achieves only a slight increase in the open-circuit voltages of solar cell devices. This process also involves high temperatures and long reaction times of between 90 to 120 minutes, which ultimately

increases the costs of the process and often makes it commercially unviable.

It has also been demonstrated, in an article by M. Marudachalam,  
5 R.W. Birkmire, H. Hichri, J.M. Schultz, A. Swartzlander and M.M.  
Al-Jassim, J. Appl. Phys. **82**(6), 1997, 2896, that homogeneous  
Cu(In,Ga)Se<sub>2</sub> thin films can be produced by annealing a phase-  
separated mixture of CuInSe<sub>2</sub> and CuGaSe<sub>2</sub> in argon in the  
temperature range of 500°C to 600°C for 60 to 120 minutes. This  
10 post-annealing step in an inert atmosphere resulted in substantial  
losses of Se from the film, which necessitated the re-introduction  
of group VI elements.

It has now surprisingly been found by the inventor that the  
15 significant problems discussed above can at least partially be  
overcome or reduced by controlling the formation of the ternary  
alloys in the selenization step such that the selenization reaction  
does not proceed to completion thereby to form a stable mixture  
of binary and ternary alloys.

20

### **Object of the Invention**

It is an object of the invention to provide a novel alternative  
process for the preparation of a group I-III-VI semiconductor film.

25

**Disclosure of the Invention**

A method for preparing a semiconductor film of a group I-III-VI quaternary or higher, the method comprising the steps of:

5

i. providing a metal film comprising a mixture of group I and group III metals;

10

ii. heat treating the metal film in the presence of a source of a first group VI element (hereinafter referred to as  $VI_1$ ) under conditions to form a first film of a stable mixture of at least one binary alloy and at least one group I-III- $VI_1$  ternary alloy, the at least one binary alloy being selected from the group consisting of group I- $VI_1$  and group III- $VI_1$  alloys;

15

20

iii. optionally heat treating the first film in the presence of a source of a second group VI element (hereinafter referred to as  $VI_2$ ) under conditions to convert the first film into a second film comprising at least one alloy selected from the group consisting of group I- $VI_1$ - $VI_2$  alloys and group III- $VI_1$ - $VI_2$  alloys; and the at least one group I-III- $VI_1$  ternary alloy of step (ii);

- iv. heat treating either the first film or second film to form a semiconductor film of a group I-III-VI quaternary or higher order alloy.

5 For the purposes of this specification the term stable shall be taken to mean that the molar ratio of the group I-VI<sub>1</sub> and/or group III-VI<sub>1</sub> species to the at least one group I-III-VI<sub>1</sub> ternary alloy remains substantially constant.

10 Step (i)

The metal film of step (i) may be provided on a substrate, which substrate is preferably inert under the reaction conditions and heat treatment steps of the above method. Suitable substrates  
15 include glass, flexible metallic, polymer foils or the like. Preferably, the substrate is from 0.05 mm to 3.0 mm thick.

The substrate may optionally be coated with a metal layer, preferably a Mo layer having a thickness of 0.5 to 1.0 μm.  
20 Preferably, the metal film is provided on the metal layer.

In a preferred embodiment of the invention, the metal film of step (i) comprises a mixture of metals selected from the group consisting of Cu, In and Ga, preferably a combination of Cu, In  
25 and Ga, which metals may be in elemental form or in the form of

an alloy. Preferably the source of Cu and Ga is an alloy, preferably  $\text{Cu}_{0.75}\text{Ga}_{0.25}$  alloy. Preferably the metal film is a Cu-In-Ga alloy. Other group III elements of interest in addition to Ga are Al and Th.

5

The metals may be deposited onto the substrate by techniques well known in the art, such as direct current (DC) magnetron sputtering, to form the metal film which may be 0.6 to 1  $\mu\text{m}$  thick, preferably 0.6  $\mu\text{m}$  thick. It will be appreciated that there are other  
10 means by which the group I and group III metals may be deposited onto the substrate such as for example by means of electro-deposition or evaporation.

15 *Step (ii)*

The metal film of step (i) is heat treated in the presence of a source of a group VI<sub>1</sub> element. Preferably VI<sub>1</sub> is Se. More preferably the source comprises an atmosphere of  $\text{H}_2\text{Se}$  and  
20 preferably at least one other gas, preferably an inert gas such as Ar. It is also envisaged that elemental Se in vapour form may also be used.

The molar concentration of Se relative to the at least one other  
25 gas, preferably Ar, may be between 0.01 to 15 molar percent

preferably between 0.02 to 1.0 molar percent and more preferably between 0.05 to 0.3 molar percent.

5 In one embodiment of the invention step (ii) is carried out under reaction conditions wherein the reaction temperature is between 300°C to 500°C, preferably between 350°C to 450°C.

1 In a preferred embodiment of the invention, the metal film of step (i) is heated rapidly to the reaction temperatures set out above.  
10 More preferably, the metal film is heated to the reaction temperatures set out above within 5 minutes.

Preferably, the metal film of step (i) is exposed to the source of the group VI<sub>1</sub> containing element for a period of between 10 to  
15 120 minutes, preferably 15 to 90 minutes and more preferably between 30 to 60 minutes.

In one embodiment of the invention, the metal film of step (i) is heat treated in the presence of a source of Se to form a first film  
20 comprising a stable mixture of binary selenides, comprising CuSe, InSe and Ga<sub>2</sub>Se<sub>3</sub> and at least one group I-III-VI ternary alloy.

Preferably the first film is Se deficient in that the first film has  
25 below 50 atomic % of Se. Preferably the first film comprises a Se

concentration of between 43 – 47 atomic %, relative to 50 atomic % required for stoichiometric fully reacted films. Preferably the Se/(Cu+Ga+In) ratio is below 1.

- 5 In a preferred embodiment of the method as defined above, the first film is subjected to a treatment step under conditions to ensure that the mixture of binary selenides and the at least one group I-III-VI ternary alloy remains stable.
- 10 Preferably, the conditions include the removal of the source of the group VI<sub>1</sub> element thereby to maintain the stability of the mixture. In a preferred embodiment, the conditions may also include the exposure of the first film to an inert atmosphere, preferably Ar, for a period of between 5 to 20 minutes, preferably
- 15 10 to 15 minutes. The first film may also be cooled, preferably to temperatures below 100°C.

*Method for the formation of a group I-III-VI pentenary alloy semiconductor film.*

20

Steps (i) and (ii) are as set out above.



*Step (iii)*

In one embodiment of the invention, the first film is heat treated in the presence of a source of a second group  $VI_2$  element, preferably so as to convert the first film into a second film comprising a group I- $VI_1$ - $VI_2$  alloy; a group III- $VI_1$ - $VI_2$  alloy and the at least one group I-III- $VI_1$  ternary alloy.

Preferably  $VI_2$  is a source of S. In a preferred embodiment of the invention, the source of S comprises a mixture of  $H_2S$  and at least one inert gas, preferably an inert gas such as Ar.

In a preferred embodiment of the invention, the molar concentration of S relative to the at least one inert gas, preferably Ar, may be between 0.1 to 10 molar percent, preferably between 0.3 and 0.5 molar percent.

The heat treatment of step (iii) may be at a temperature of between  $100^{\circ}C$  to  $500^{\circ}C$ , preferably  $400^{\circ}C$  to  $500^{\circ}C$ , more preferably  $450^{\circ}C$  for a period of between 5 to 10 minutes, preferably 5 minutes.

In a preferred embodiment of the invention and where  $VI_1$  in step (ii) is a source of Se, the second film may be subjected to the heat treatment of step (iii), wherein  $VI_2$  is S, so as to convert the

first film to a second film comprising a mixture of sulfoselenides and the at least one group I-III-VI ternary alloy, the sulfoselenides being selected from the group consisting of Cu(Se,S), In(Se,S) and Ga(Se,S), preferably all three of them.

- 5 Preferably there are two Group I-III-VI<sub>1</sub> ternary alloys, preferably CuGaSe<sub>2</sub> and CuInSe<sub>2</sub>.

*Step (iv)*

- 10 In a preferred embodiment of the invention, the second film of step (iii) may be annealed, preferably in the presence of a source of S, for a period of between 5 to 10 minutes, preferably 5 minutes at a temperature of between 450°C to 600°C, preferably 500°C to 550°C, more preferably 500°C, such that at least one
- 15 alloy selected from the group consisting of group I-VI<sub>1</sub>-VI<sub>2</sub> and group III-VI<sub>1</sub>-VI<sub>2</sub> alloys reacts with the at least one group I-III-VI<sub>1</sub> alloy to form at least one group I-III-VI quaternary alloy comprising either two group III metals or two group VI elements, namely VI<sub>1</sub> and VI<sub>2</sub>.

20

Preferably the sulfoselenides react with the at least one group I-III-VI<sub>1</sub> ternary alloy, preferably with both group I-III-VI<sub>1</sub> ternary alloys of CuInSe<sub>2</sub> and CuGaSe<sub>2</sub> to produce a mixture of CuIn(Se,S)<sub>2</sub> and CuGa(Se,S)<sub>2</sub>.

25

Preferably the resultant mixture is annealed for 15 to 90 minutes, more preferably 30 minutes to a temperature of between 500°C to 600°C, preferably 520°C to 580°C, more preferably at 550°C to form a pentenary alloy having the general formula I:

5



wherein preferably x may vary between 0.1 and 0.5, preferably  
10 between 0.25 and 0.3 and y may preferably vary between 0 and 1, more preferably between 0.05 and 0.5.

The pentenary alloy is preferably a homogeneous film and may preferably be annealed for an additional 15 minutes to optimise  
15 the structural properties of the pentenary alloy. The homogeneous film may be between 1.5 µm to 2.0 µm thick.

*Method for the formation of a group I-III-VI quaternary alloy semiconductor film.*

20

Step (i) and step (ii) are the same as discussed above and step (iii) is not carried out.

*Step (iv)*

In one embodiment of the invention, the first film of step (ii) is heat treated in an inert atmosphere, preferably an Ar containing atmosphere.

Preferably, the first film of step (ii) may be annealed in an Ar containing atmosphere at a temperature of between 100°C to 600°C, preferably between 200°C to 550°C, more preferably between 500°C and 550°C for 10 to 60 minutes, preferably between 15 and 30 minutes.

In a preferred embodiment of the invention, the first film is then annealed in the presence of a source of a Group VI<sub>1</sub> element, where VI<sub>1</sub> is preferably Se as in step ii. The first film is annealed preferably 10 to 60 minutes, more preferably 30 minutes to form a quaternary alloy, namely Cu(In,Ga)Se<sub>2</sub>. Preferably the source of Se is an atmosphere of H<sub>2</sub>Se and at least one other gas, preferably an inert gas such as Ar. Preferably the molar concentration of Se relative to the at least one other gas is 0.06%.

Preferably the quaternary alloy is homogeneous.

It is preferable when forming the quaternary alloy that step (ii) be carried out at a temperature of 350°C to 450°C, preferably 400°C such that the first film comprises a stable mixture of binary selenides, selected from the group consisting of CuSe, InSe and Ga<sub>2</sub>Se<sub>3</sub>; and a single ternary alloy, namely CuInSe<sub>2</sub>.

According to a second aspect of the invention there is provided a method for the production of a group I-III-VI pentenary alloy semiconductor film comprising the steps of:

10

(i) providing a metal film comprising a mixture of Cu, In and Ga on a substrate;

15

(ii) heat treating the metal film in the presence of a source of Se under conditions to form a first film comprising a stable mixture of CuSe, InSe, Ga<sub>2</sub>Se<sub>3</sub> and at least one ternary alloy selected from the group consisting of, CuInSe<sub>2</sub> and CuGaSe<sub>2</sub>;

20

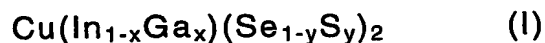
(iii) heat treating the first film in the presence of a source of S under conditions to convert the first film into a second film comprising a mixture of sulfoselenides, namely Cu(Se,S), In(Se,S) and Ga(Se,S) and the at least one ternary alloy;

25

- (iv) heat treating the second film of step (iii) to react the said mixture to form a pentenary alloy of Cu, In, Ga, Se and S.

Preferably the pentenary alloy has the formula I:

5



preferably x may vary between 0.1 and 0.5, preferably between 0.25 and 0.3 and y may be between 0 and 1, preferably between  
10 0.05 and 0.5.

The method according to the second aspect of the invention, wherein the first film is preferably subjected to a treatment step under conditions to ensure that the mixture of binary selenides  
15 and the ternary alloys remains stable.

According to a third aspect of the invention there is provided a method for the production of a group I-III-IV quaternary alloy semiconductor film comprising the steps of:

20

- (i) providing a metal film comprising a mixture of Cu, In and Ga on a substrate;

- (ii) heat treating the metal film in the presence of a source  
25 of Se under conditions to form a first film comprising a

stable mixture of binary alloys, and at least one ternary alloy, the binary alloys comprising CuSe, InSe and Ga<sub>2</sub>Se<sub>3</sub>, and the at least one ternary alloy being selected from the group consisting of CuInSe<sub>2</sub> and CuGaSe<sub>2</sub>

5

(iii) heat treating the first film of step (ii) to form an alloy of Cu, In, Ga and Se.

Preferably the quaternary alloy is Cu(In,Ga)Se<sub>2</sub>.

10

The method according to the third aspect of the invention, wherein step (ii) is preferably carried out at a reaction temperature of about 400°C such that the first film comprises a stable mixture of the binary selenides and CuInSe<sub>2</sub>.

15

Preferably the first film is subjected to a treatment step under conditions to ensure that the mixture of binary selenides and the ternary alloys remains stable.

## Detailed Description of the Invention

Without thereby limiting the scope of the invention and by means of example only embodiments of the invention will now be described by means of the following examples. In the examples reference is made to the accompanying figures:

Figures 1.1 - 1.2 are X-ray diffraction spectra (Cu  $K_{\alpha}$  radiation) of the first film formed according to step ii of example 1. More particularly figure 1.1 is an XRD pattern of the first film of sample 200250-a and figure 1.2 is an XRD pattern of the first film of sample 200251-a;

Figure 2 are X-ray diffraction spectra (Cu  $K_{\alpha}$  radiation) depicting the crystalline nature of the resultant second film of sample 200251-a, which were formed according to steps iii and iv of example 1, illustrating the transitions from the ternary to the quaternary and pentenary alloy states;

Figures 3.1-3.2 are GIXRD patterns of the [112] peak positions of the homogeneous pentenary



alloys of samples 200251-a and 200250-a in comparative example 1, measured with Cu  $K_{\alpha}$  radiation;

Figure 4

is a plot of open-circuit voltage ( $V_{oc}$ ) for a number of photovoltaic cells having semiconductor absorber films of sample 200251-a as set out in example 2;

Figure 5.1-  
5.2

are XRD patterns (Cu  $K_{\alpha}$  radiation) of a graded quaternary alloy of comparative example 2 and a homogeneous quaternary alloy of comparative example 2;

Figure 6

are GIXRD patterns of the [112] peak position of the homogeneous quaternary alloy of comparative example 2. The correspondence in the lattice parameters as function of sample depth indicates that the film is homogeneous rather than compositionally graded;

Figure 7.1-

7.2

are X-ray fluorescence profiles depicting the in-depth composition properties of the graded quaternary alloy and homogeneous quaternary alloy of comparative example 2 respectively.

#### General Experimental Procedure

5 It is well known to those skilled in the art that photovoltaic cells include a substrate for supporting a semiconductor film. Typically, any suitable substrate may be used, which substrate does not react with the semiconductor film and which does not modulate the semiconductor properties. Suitable substrates include glass,  
10 flexible metallic or polymer foils and the like.

The substrate may have a thickness of 0.05 to 3.0 mm and is often coated with a metal layer of molybdenum in order to enhance the adhesion of a resultant semiconductor film to the  
15 substrate and to serve as a contact in a completed photovoltaic device.

The thickness of the Mo coating is usually between 0.5 to 1.0  $\mu\text{m}$  and is deposited onto the substrate by DC magnetron sputtering

at a working pressure of between 0.1 to 0.8 Pa. It will be appreciated that there are many other techniques known in the art which relate to the use and deposition of metal layers, for example there may be more than one layer, or chromium may be  
5 used in place of molybdenum.

*Step (i) of the method according to the invention*

For purposes of the experiment, a 2 mm thick soda lime glass  
10 substrate was used. The substrate was cleaned in an ultrasonically stirred soap solution for 10 minutes by gently moving the substrate placed in a holder. The substrate was then held under a cold deionised water tap for a few minutes to ensure the removal of excess soap thereon. Thereafter, the substrate  
15 was cleaned in an ultrasonically stirred deionised hot water bath by gently moving the substrate holder. Finally, the substrate was dried for 10 minutes in dry-nitrogen in an oven maintained at 120°C.

20 Once dried, a Mo layer was deposited onto the substrate. This was followed by co-sputtering the metal film of Cu, Ga and In onto the Mo layer. The deposition of Mo and the co-sputtering were carried out in a DC magnetron sputtering unit consisting of a deposition chamber which accommodates three 9 inch circular  
25 cathodes (targets): Mo, pure In and a  $\text{Cu}_{0.75}\text{Ga}_{0.25}$  alloy target.

The deposition chamber was evacuated to a base pressure of  $5 \times 10^{-5}$  Pa for at least three hours. The Mo layer was deposited without any intentional heating of the substrate at a working pressure of 0.5 Pa, using Ar as plasma gas. The total thickness of the Mo layer was 1  $\mu\text{m}$ .

The deposition of the Mo layer was followed, without breaking vacuum, by the co-sputtering of  $\text{Cu}_{0.75}\text{Ga}_{0.25}$  and In at a working pressure of 0.3 Pa. The co-sputtering was also carried out without intentional substrate heating and the substrate was rotated during co-sputtering in order to enhance the mixing of the Cu-Ga-In alloy. The total thickness of the Cu-In-Ga alloys was 0.6  $\mu\text{m}$  and the Cu/(In+Ga)- and Ga/(Ga+In)- atomic ratios were maintained at 0.9 and 0.25 respectively.

#### Example 1: Experimental procedure for the production of a group

##### I-III-VI pentenary alloy

#### *Step ii of the method according to the invention*

The substrate with the co-sputtered metal film of step i was placed in a horizontal quartz tube reactor (herein after referred to as the reactor tube). The substrate was laid on a graphite substrate holder and placed in the reactor tube. Graphite

substrate holders were used to ensure the uniform heating of the substrate.

5 The reactor tube was evacuated to a pressure of  $2.67 \times 10^{-4}$  Pa for at least two hours before carrying out step ii. The reaction tube was then pressurised and a constant Ar flow of 1300 standard cubic centimetres per minute (hereinafter referred to as sccm) was established and maintained during the reaction process.

10 Once a constant inert gas flow was established, the temperature of the substrate with the metal film was ramped up to the reaction temperatures set out in Table 1 below over a period of 5 minutes. The reaction gas mixture (0.06 molar %  $\text{H}_2\text{Se}$  in Ar) was passed through the reactor tube while the substrate was heated to the  
15 reaction temperatures set out in Table 1 for the reaction periods also set out in Table 1 so as to form a first film comprising a stable mixture of binary selenides, namely  $\text{CuSe}$ ,  $\text{InSe}$  and  $\text{Ga}_2\text{Se}_3$  and at least one of the following ternary alloys, namely  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$ . The presence of one or both of the  
20 ternary alloys is dependent upon the reaction temperature of step ii.

Referring to figure 1.1 which is an XRD pattern of the first film of step ii prepared under the reaction conditions set out in Table 1  
25 for sample 200250-a, it is clear that there is present a mixture of

the three binary selenides and  $\text{CuInSe}_2$ . Under the reaction conditions for sample 200250-a, there is no evidence of the formation of  $\text{CuGaSe}_2$  at  $400^\circ\text{C}$ .

- 5 Referring to figure 1.2 which is an XRD pattern of the first film of step ii prepared under the reaction conditions set out in Table 1 below for sample 200251-a, reflections [112], [220/204] and [312/116] comprise (a) relatively sharply defined peak positions corresponding to  $\text{CuInSe}_2$  and (b) shoulders resulting from the  
10 presence of  $\text{CuGaSe}_2$  and the remaining binary selenides of  $\text{CuSe}$  and  $\text{Ga}_2\text{Se}_3$ .

Upon the termination of the reaction periods as set out in Table 1, the samples were subjected to a treatment step in order to further  
15 maintain the stability of the resultant stable mixture. This was done by terminating the flow of  $\text{H}_2\text{Se}$  in the reaction tube and by rapidly cooling the samples to temperatures of below  $100^\circ\text{C}$ . The samples were kept under the above conditions for 15 minutes to ensure the complete removal of the  $\text{H}_2\text{Se}$  species from the reactor  
20 tube.

Both figures 1.1 and 1.2 depict a stable mixture wherein the reaction conditions set out in Table 1 below prevent the reaction going to completion and thus forming fully reacted ternary alloys

of  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$  in the absence of  $\text{CuSe}$ ,  $\text{InSe}$  and  $\text{Ga}_2\text{Se}_3$ .

5 It is believed by the inventor that starving the system of Se by using extremely low concentrations of Se, and by using low temperatures so as to prevent the completion of the selenization reaction to form fully reacted ternary alloys, stable mixtures such as those represented in figures 1.1 or 1.2 can be achieved.

10 Table 1: Reaction conditions (temperature and time) for step ii according to the invention.

Reaction conditions	
Sample	( $\text{H}_2\text{Se}/\text{Ar}$ )
200248-c	400°C/20min
200250-a	400°C/30min
200263-a	400°C/40min
200371-a	400°C/60min
200251-a	450°C/30min

*Step iii according to the method of the invention*

15

The first film of step ii formed under the reaction conditions in Table 1 above was then heated in the reaction tube in an atmosphere containing a mixture of  $\text{H}_2\text{S}$  and Ar (the molar percentage of S in the reactive mixture being maintained close to

0.35% relative to Ar) at a reaction temperature of 450°C for a period of 5 minutes such that the binary selenides react with S to convert the first film of step ii into a second film comprising a mixture of sulfoselenides, namely Cu(Se,S), In(Se,S) and Ga(Se,S) and the ternary alloys.

Referring to Figure 2 which is a XRD pattern of sample 20051-a, and in particular the XRD for step iii, the presence of In(Se,S) is visible, however the remaining sulfoselenides of Cu(Se,S) and Ga(Se,S) are not shown in the selected 2θ range. The inventor believes that at temperatures around 450°C, and as depicted in the XRD for step iii, the reaction between the existing S species in the gaseous atmosphere and the ternary alloys (indicated by peaks 1 at 26.71° and 2 at 27.75° in fig. 2) is substantially insignificant. In other words, the reaction between S and the ternary alloys is insignificant at this specific temperature.

*Step iv according to the method of the invention*

The second film of step iii was then subjected to the following heat treatment steps in the reaction tube:

(a) annealing the second film of step iii at temperatures of about 500°C for 5 minutes, such that the sulfoselenides react with the ternary alloys to produce quaternary



CuIn(Se,S)<sub>2</sub> and CuGa(Se,S)<sub>2</sub> alloys (indicated by peaks 3 at 27.01° and 4 at 28.05° in the XRD for step iv(a)).

5 It is believed by the inventor that in the event that step ii is carried out at 400°C, and thus in the absence of CuGaSe<sub>2</sub>, the sulfoselenides may directly react to form CuGa(Se,S)<sub>2</sub> in this step. However, under the latter experimental conditions the resulting quaternary alloy will contain a higher S concentration, resulting in a shift of peak 4 to a  
10 higher 2θ value than that indicated in the XRD pattern for step iv(a).

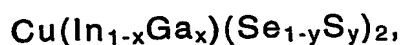
The reaction of S with the group I-III-VI<sub>4</sub> ternary alloys is represented by the absence of the sulfoselenides for  
15 example, the absence of the In(Se,S) peak in the XRD pattern for step iv(a) in figure 2 is indicative of the fact that it has reacted with CuInSe<sub>2</sub> to form CuIn(Se,S)<sub>2</sub>.

20 Comparing the XRD for step iii in figure 2 with the XRD for step vi(a) in figure 2, it is clear from the subsequent 2θ shift that the ternary alloys (represented by [112] peaks 1 and 2) have reacted with the sulfoselenides to form the quaternary alloys CuIn(Se,S)<sub>2</sub> and CuGa(Se,S)<sub>2</sub> (represented by [112] peaks 3 and 4).

The degree of shift of the [112] peak from position 1 to 3, and 2 to 4, is determined by the volume fraction of sulfoselenides available to react with the ternary alloys. The volume fraction sulfoselenides is in turn dependent on the volume fraction binary selenides present in the first film of step ii. Once the stable fully reacted quaternary alloys are formed around 500°C, the reaction process becomes diffusion limited and further reaction to H<sub>2</sub>S/Ar at 500°C for extended periods has insignificant influences on the crystalline state and S content of the composite alloy.

(b) Annealing the resultant composite alloy in the reaction tube from (a) above at a temperature of 550°C for a period of 15 minutes. The transition from the quaternary to pentenary alloy state (indicated by peak 5 at 27.2° in the XRD for step iv(b) in Fig. 2) occurs within 10 to 15 minutes of the reaction with H<sub>2</sub>S, while an additional 15 minutes of annealing is typically required to optimize the structural properties of the pentenary alloy.

The homogeneous pentenary alloys have typical thickness of between 1.5 and 2 μm and may be described by the chemical formula:



wherein  $x$  may vary between 0.1 and 0.5, preferably between 0.25 and 0.3 and  $y$  may be between 0 and 1, preferably between 0.05 and 0.5.

5

Both steps iii and iv are carried out consecutively in a reactive gas mixture of  $H_2S$ , wherein the temperature is ramped up from 450°C to 550°C.

10 Upon the completion of both steps iii and iv, the reaction tube was evacuated to a pressure of  $2.67 \times 10^{-4}$  Pa for at least two hours to ensure the complete removal of toxic gases from the reactor tube. The tube was then pressurized and the samples were removed.

15

#### Comparative Example 1 – pentenary alloys

The samples set out in Table 1 above were subjected to steps iii  
20 and iv to form homogeneous semiconductor pentenary alloys and their corresponding chemical compositions as determined by energy dispersive x-ray spectroscopy (EDS) with reference to  $Cu/(In+Ga)$ ,  $Ga/(Ga+In)$ , and  $S/(Se+S)$  atomic ratios are set out in Table 2 below. Also shown in Table 2 below are the band gap  
25 values for each of the samples as well as the position of the [112] diffraction peaks.

Table 2: Summary of reaction conditions<sup>†</sup> and their influence on the degree of sulfur incorporation and the resulting band gap values of the respective samples.

Sample	Step II reaction condition s H <sub>2</sub> Se/Ar	Step IV reaction conditions H <sub>2</sub> S/Ar	Cu/In+Ga	Ga/Ga+In	S/Se+S	2 $\theta_{(112)}$	E <sub>g</sub> (eV)
200248-c	400°C/ 20min	550°C/ 30min	0.90	0.25	0.56	27.65	1.39
200250-a	400°C/ 30min	550°C/ 30min	0.91	0.25	0.45	27.55	1.32
200263-a	400°C/ 40min	550°C/ 30min	0.90	0.25	0.32	27.30	1.23
200371-a	400°C/ 60min	550°C/ 30min	0.93	0.25	0.10	27.0	1.15
200251-a	450°C/ 30min	550°C/ 30min	0.92	0.24	0.23	27.20	1.20
200252-a	450°C/ 30min	550°C/ 90min <sup>‡</sup>	0.91	0.23	0.25	27.21	1.21

5

<sup>†</sup>These studies were conducted in a constant flow of 0.06% H<sub>2</sub>Se diluted in Ar and 0.35% H<sub>2</sub>S diluted in Ar. The 2 $\theta$ - positions of the [112] peaks of the pentenary alloys were measured by GIXRD with a Cu tube at 40kV. The corresponding band gap values were calculated from quantum efficiency measurements. <sup>‡</sup> The time period for step vi(b) was increased to 90 minutes.

10

A comparison of the first four samples in Table 2 clearly indicates the influence of the conditions of step ii of the invention on the

degree of sulfur incorporation which is set out in the S/(S+Se) column of the table. Accordingly, changing the conditions of step ii modified the subsequent reaction kinetics during step iii of the invention resulting in a change in the sulfur incorporation in the  
5 final  $\text{Cu}(\text{In}_{0.75}\text{Ga}_{0.25})(\text{Se}_{1-y}\text{S}_y)_2$  semiconductor film.

A comparison of sample # 200250-a and # 200251-a, indicates how an increase in the reaction temperature of step ii from 400°C to 450°C led to a substantial decrease in the sulfur incorporation  
10 and hence a shift in the [112] diffraction peak to a lower angle.

In the case of the last two samples, (i.e. 200251-a and 200252-a) the reaction conditions of step ii were maintained constant, while the reaction periods for annealing the resultant composite alloy in  
15 step iv(b) above was increased from 30 to 90 minutes. Comparison of these samples clearly indicates that annealing in the presence of an  $\text{H}_2\text{S}/\text{Ar}$  atmosphere for extended periods above 30 minutes had marginal influences on the degree of sulfur incorporation.

20

Accordingly this indicates that the pentenary alloy is formed after only 30 minutes of annealing in  $\text{H}_2\text{S}/\text{Ar}$  at 550°C therefore implying that once the fully reacted homogeneous pentenary alloys are produced, the reaction process becomes diffusion

limited and further incorporation of sulfur needs to occur via the replacement of selenium species.

Figures 3.1 and 3.2 are grazing-incidence x-ray diffraction (GIXRD) patterns of the [112] reflections of samples 200251-a, 200250-a set out in Table 2 above. In this characterization method, decreasing amounts of the incident angle result in a decreasing penetration depth of the x-ray beam. It is important to note that scattering angles between  $0.2^\circ$  and  $10^\circ$  revealed virtually no shift in the lattice parameters between the surface and bulk material, which confirms the homogeneity of the pentenary alloys. Of equal significance is that the variation in the conditions of step ii resulted in a dramatic shift in the  $2\theta$ - position of the [112] diffraction peaks. Since the gallium content is virtually constant in all composite alloys, this relative shift is attributed to the varying degrees of sulfur incorporation.

Example 2: Determination of the open-circuit voltages for various solar cell devices comprising homogeneous pentenary alloys as absorber films.

Solar cells devices were fabricated according to a standard cell fabrication procedure, which included a 50 nm CdS buffer layer and a 50 nm intrinsic ZnO/150 nm indium tin oxide (ITO) window layer. The glass/Mo/Cu(In,Ga)(Se,S)<sub>2</sub>/CdS/ZnO cell structures

were evaluated under simulated A.M. 1.5 conditions at 25°C. The band gap values of the homogeneous pentenary alloys were varied by modifying the reaction conditions of step ii, as indicated in Table 2. The corresponding cell parameters are set out in

5 Table 3 below.

Table 3: Summary of the cell parameters of various photovoltaic devices in which the absorber films are homogeneous pentenary alloys with different band gap values.

10

Samples	Ga/Ga+In	S/Se+S	E <sub>g</sub> eV	V <sub>oc</sub> mV	J <sub>sc</sub> mA/cm <sup>2</sup>	FF %	η %
200248-c	0.25	0.56	1.39	677.9	23.55	53.3	8.5
200250-a	0.25	0.45	1.32	685.9	27.17	59.8	11.2
200252-a	0.23	0.25	1.21	630.2	29.46	64.1	11.9
200251-a	0.24	0.23	1.20	610.4	32.86	67.5	13.5

The conversion efficiencies were critically related to the band gap of the pentenary alloys and varied between 8% and 14%, the best device being that with the lowest band gap (sample 200251-a). All devices had open-circuit voltages (V<sub>oc</sub>) beyond 600 mV. Also, 24 photovoltaic cells were made from pentenary alloys prepared under the reaction conditions set out above for sample 200251-a. The V<sub>oc</sub> values of these cells were confined to values in the range of 600 to 640 mV (see fig. 4). This is clear evidence of the reproducibility of the method according to the invention.

20

Example 3: Experimental procedure for the production of a group

I-III-VI quaternary alloy

Step i is the same as set out under general experimental  
5 procedure.

*Step ii of the method according to the invention*

In this case the same method as set out in step ii above was  
10 followed, however the reaction temperature was kept at 400°C so  
as to form a first film comprising a stable mixture of binary  
selenides and  $\text{CuInSe}_2$  only.

It is believed by the inventor that in the case of the production of  
15 quaternary alloy semiconductor films it is necessary to prevent  
the formation of the second ternary alloy, namely  $\text{CuGaSe}_2$  so as  
to obtain a homogeneous quaternary alloy. This was achieved by  
keeping the reaction temperature at 400°C.

20 As above, the first film of step ii is subjected to a treatment step  
to maintain the stability of the mixture, wherein the  $\text{H}_2\text{Se}$  flow is  
terminated and the first film is cooled to temperatures below  
100°C. The Ar flow in this case was maintained for a period of at  
least 15 minutes, once again to ensure the complete removal of  
25 the  $\text{H}_2\text{Se}$  species.



*Step iii of the method according to the invention*

In the case of the production of a quaternary alloy semiconductor film, this step is not carried out.

5

*Step iv of the method according to the invention*

The first film is subjected to the following consecutive steps:

- 10 (a) heating the first film in the reaction tube in an inert atmosphere of Ar to a reaction temperature of 500°C for 5 minutes ;
- (b) annealing the first film in the reaction tube in an Ar  
15 containing atmosphere at 500°C for at least 15 minutes;
- (c) annealing the first film in the presence of 0.06 molar  
percent of H<sub>2</sub>Se in Ar for 30 minutes at 500°C
- 20 to form a homogeneous quaternary alloy semiconductor film.

As in the case of the formation of a pentenary alloy, the reaction tube was evacuated to a pressure of  $2.67 \times 10^{-4}$  Pa for at least two hours to ensure the complete removal of toxic gases from the

reactor tube. The tube was then pressurized and the samples were removed.

### Comparative Example 2 – quaternary alloys

5

Figures 5.1 and 5.2 represent XRD patterns, depicting the crystalline features of a typical graded quaternary alloy and a homogeneous quaternary alloys respectively, the alloys being prepared in the manner set out below. In both cases,  
10 measurements were taken with Cu K $\alpha$  radiation at 40kV.

In the case of the graded quaternary alloy (see XRD pattern in Fig. 5.1), the alloy was rapidly heated in less than 5 minutes to 500°C in the presence of H<sub>2</sub>Se, followed by an annealing step in 5  
15 molar percent H<sub>2</sub>Se in Ar for 60 minutes at 500°C. This procedure resulted in a significant degree of interdiffusion between the In-rich and Ga-rich phases and XRD analysis indicated the presence of a graded CuIn<sub>x</sub>Ga<sub>1-x</sub>Se structure. This phenomenon is represented by the asymmetric broadening of [112], [220/204] and  
20 [312/116] diffraction peaks. In this regard it is important to note that the position of the [112] diffraction peak at 26.65° still represents the lattice parameters of the pure CuInSe<sub>2</sub> phase, while the shoulder is due to increasing amounts of Ga which extend all the way to the peak position of CuGaSe<sub>2</sub>. It is therefore  
25 reasonable to assume that the surface of the absorber film

contains pure  $\text{CuInSe}_2$  and that the gallium increases gradually towards the Mo back contact.

The second sample, i.e. the homogeneous quaternary alloy, was prepared under the described experimental conditions set out in steps i, ii and iv for quaternary alloys. In order to control the reaction velocities of the binary selenides, step ii was carried out at  $400^\circ\text{C}$ , using extremely low gas concentrations of 0.06 molar %  $\text{H}_2\text{Se}$  in Ar. The reaction period was fixed at 30 minutes. After complete removal of Se species from the reaction zone, the first film was annealed in the presence of Ar for 15 minutes at a temperature of  $500^\circ\text{C}$ , followed immediately by an annealing step in 0.06 molar percent  $\text{H}_2\text{Se}$  in Ar for 30 minutes.

XRD studies of the homogeneous quaternary alloy, which is represented by Fig. 5.2, revealed that the resultant film was single-phase with no evidence of segregated material. The sharp, well-defined chalcopyrite peaks are indicative of high crystalline quality. It is also important to note that the [112] peak position increased from about  $26.65^\circ$ , which is typical for pure  $\text{CuInSe}_2$  (as shown in Figure 5.1), to a  $2\theta$  value of  $26.95^\circ$ . The latter shift of the chalcopyrite reflection towards a larger  $2\theta$  value is in accordance with a decrease in the lattice parameter associated with an increase in Ga content in the quaternary system. This degree of shift of the diffraction peaks towards higher  $2\theta$  values

is exactly in accordance with Vegard's law, assuming single-phase material and a Ga/(Ga+In) atomic ratio close to 0.25.

Figure 6 depicts GIXRD patterns of the [112] peak of the homogeneous quaternary alloy at incident angles between 0.5° and 10°. Once again it should be realized that a decrease in the incident angle results in a decrease in penetration depth of the x-ray beam. It is important to note from Fig. 6 that scattering angles between 0.5° and 10° revealed virtually no shift in the lattice parameters between the surface and bulk material, which confirms that the film is uniform rather than compositionally graded.

The in-depth compositional features of the quaternary alloys were studied by x-ray fluorescence (XRF). In this characterization method, the quaternary alloys were repeatedly etched in bromine methanol, followed by XRF  $K_{\alpha 1,2}$  line intensity measurements of the remaining material after each etching step. From these analyses the chemical compositions of the graded film and homogeneous films represented in Fig 5.1. and Fig 5.2 could be estimated through almost the entire film thickness.

Figure 7.1 represents the in-depth compositional uniformity of the compositionally graded  $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$  alloys film of Fig 5.1. It is important to note from Fig. 7.1 that the Cu and Se element

concentrations remained virtually constant through the entire thickness of the film. Even more significant, it can be seen that the remaining material after the successive etching steps became increasingly gallium-rich, while an opposite trend was observed for indium. The resulting Ga/(Ga+In) atomic ratio increased from a value of 0.28 for the sample before etching to 0.75 after the last etching step. This continuous increase in the Ga/(Ga+In) atomic ratio with sample depth is consistent with the graded  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$  phase observed by the XRD studies in Fig. 5.1.

Figure 7.2 represents the in-depth compositional properties of the homogeneous film. It can be seen that the Cu, In, Ga and Se concentration remained virtually constant through the entire layer thickness of these specific quaternary alloys. These results are therefore in line with the XRD data presented in Fig. 5.2, confirming that this growth process eliminated the grading of gallium and indium in the  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$  phase and resulted in a homogeneous quaternary alloy.

The above are only embodiments of the invention and it will be appreciated that many variations in detail are possible without thereby departing from the scope and spirit of the invention.

Dated this 14 day of August 2003

  
Patent Attorney / Agent for the Applicant

• • • 2003/6316

Figure 1.1

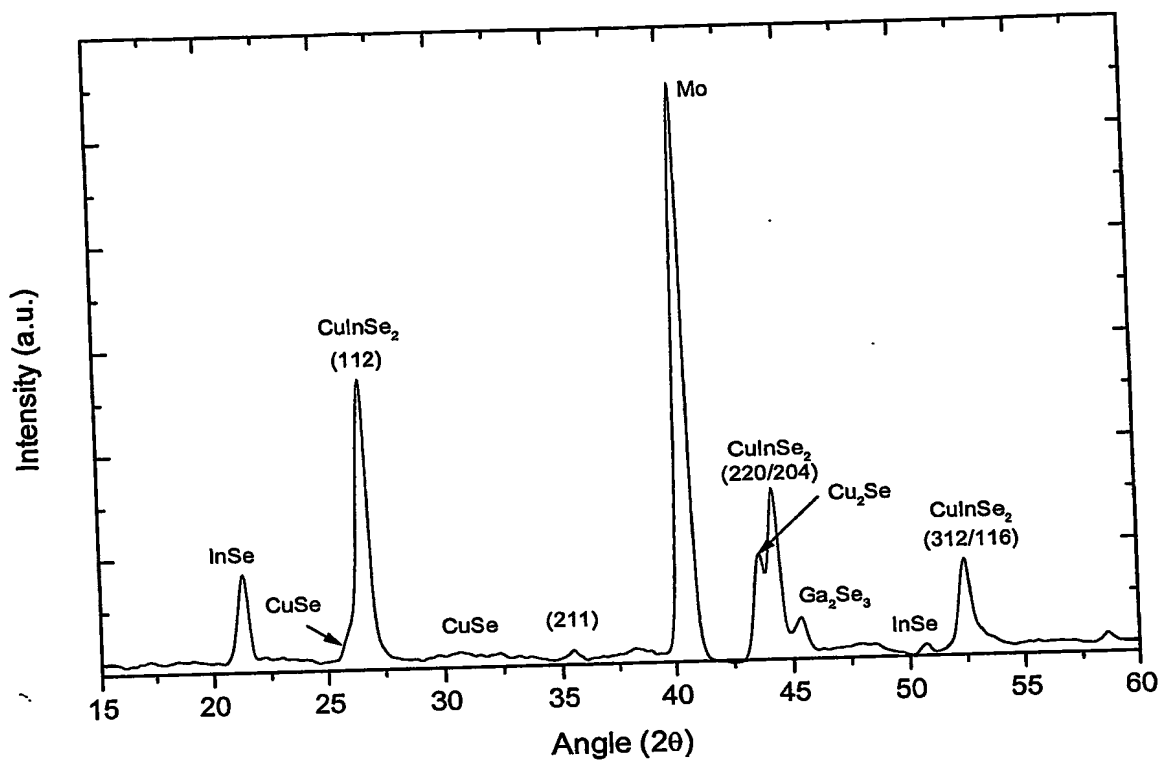


Figure 1.2

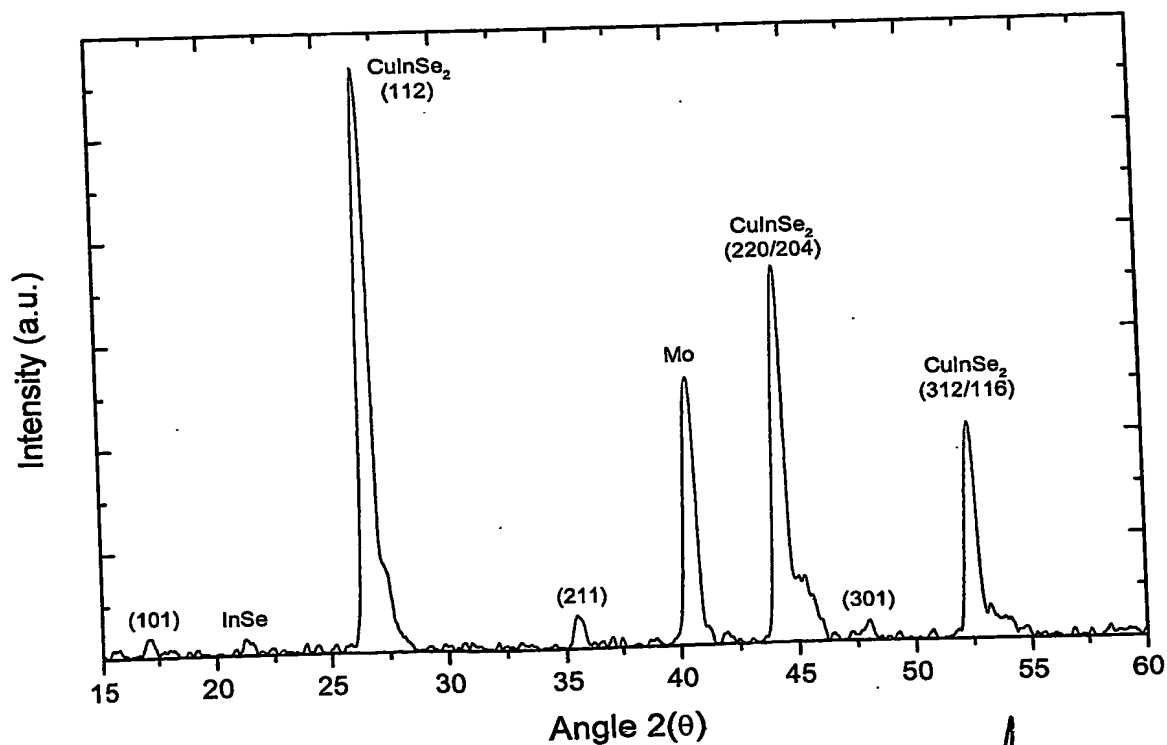


Figure 2

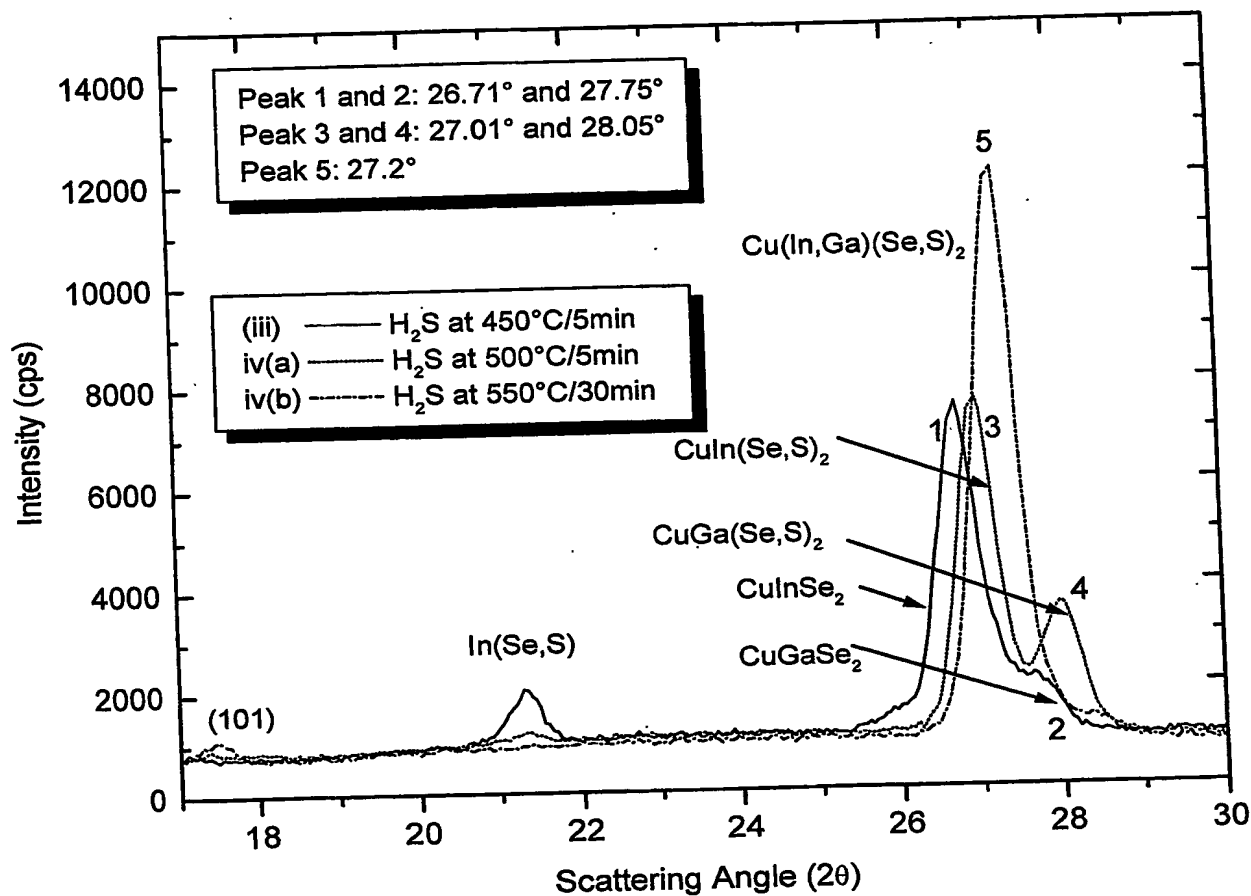


Figure 3.1

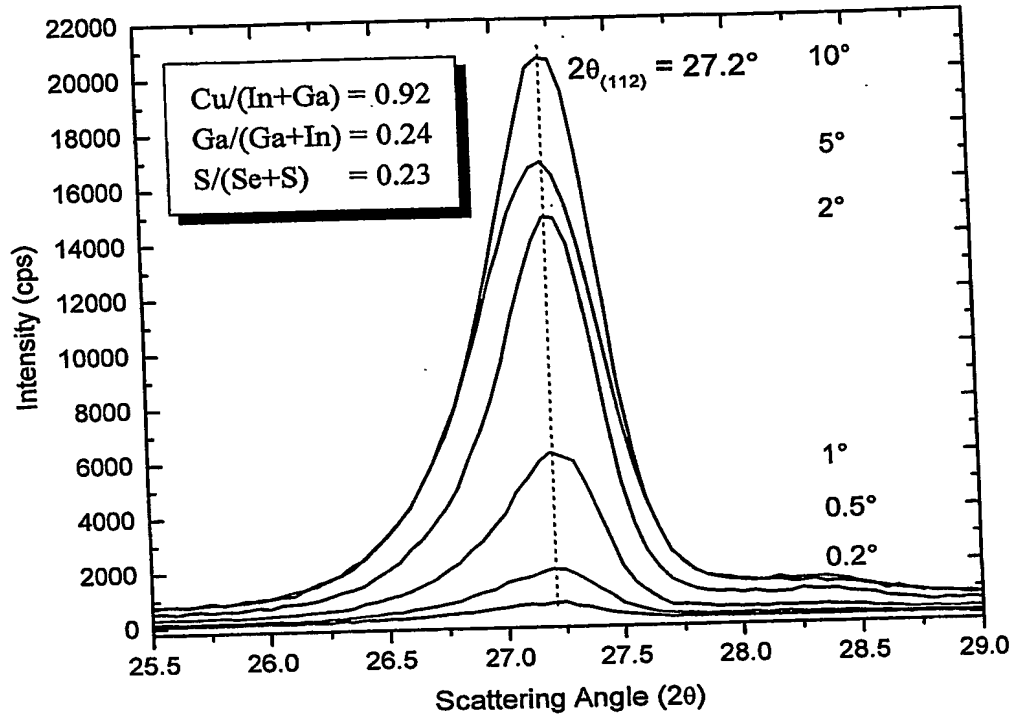
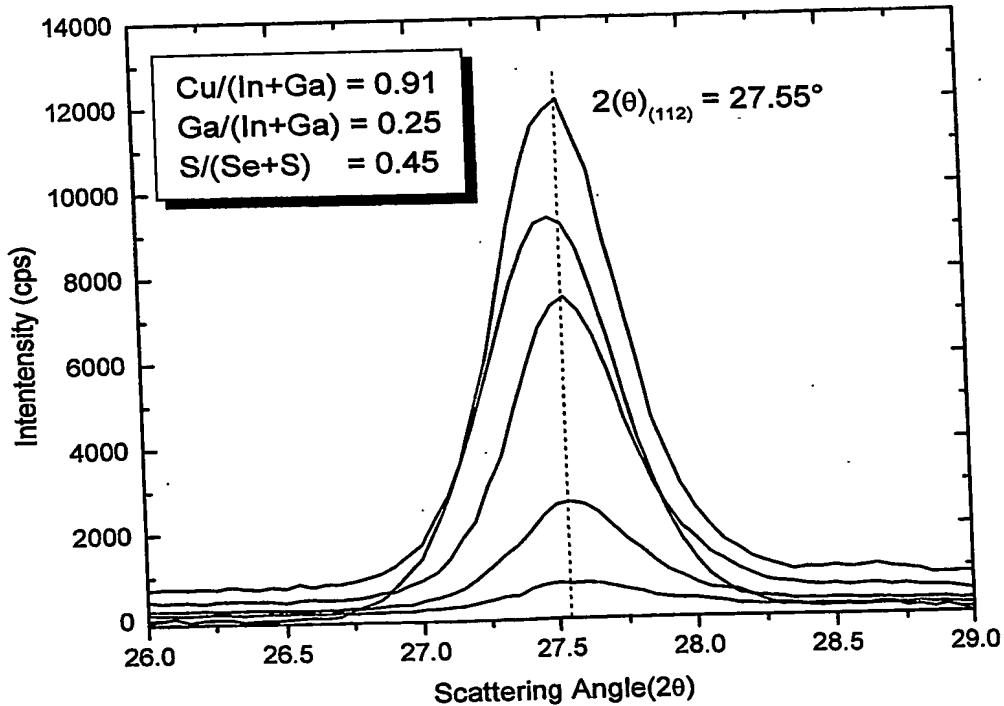


Figure 3.2





2003/6316

Figure 4

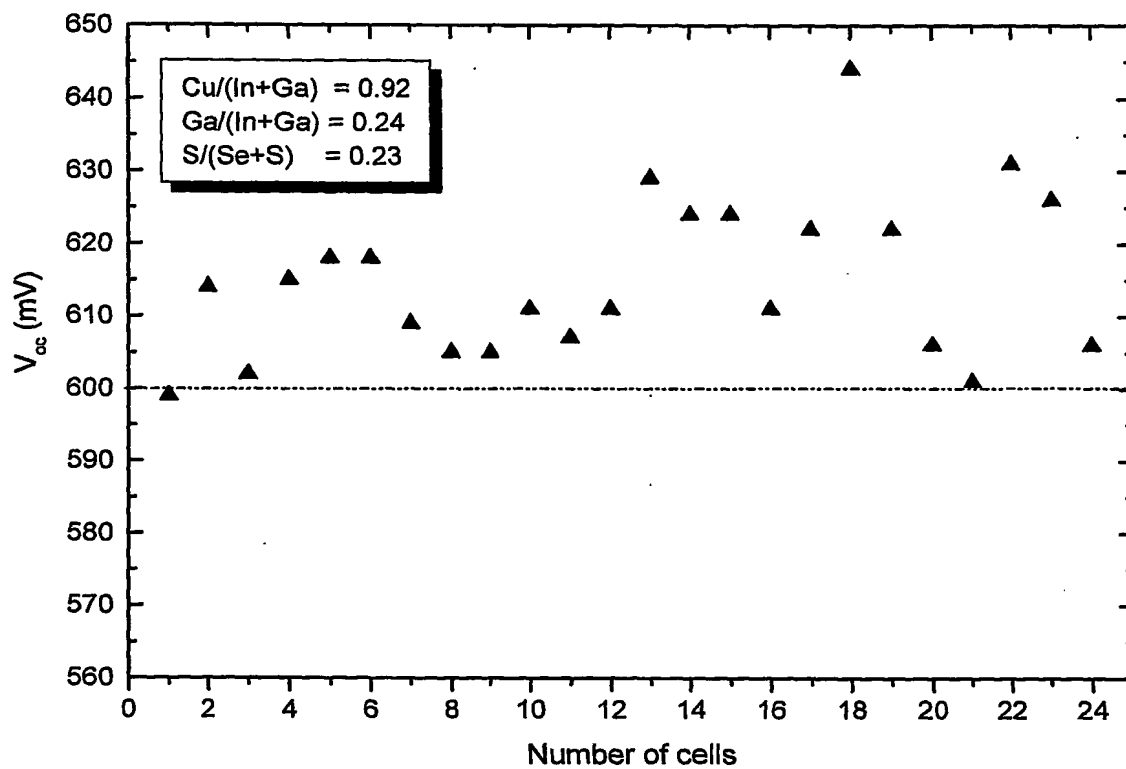


Figure 5.1

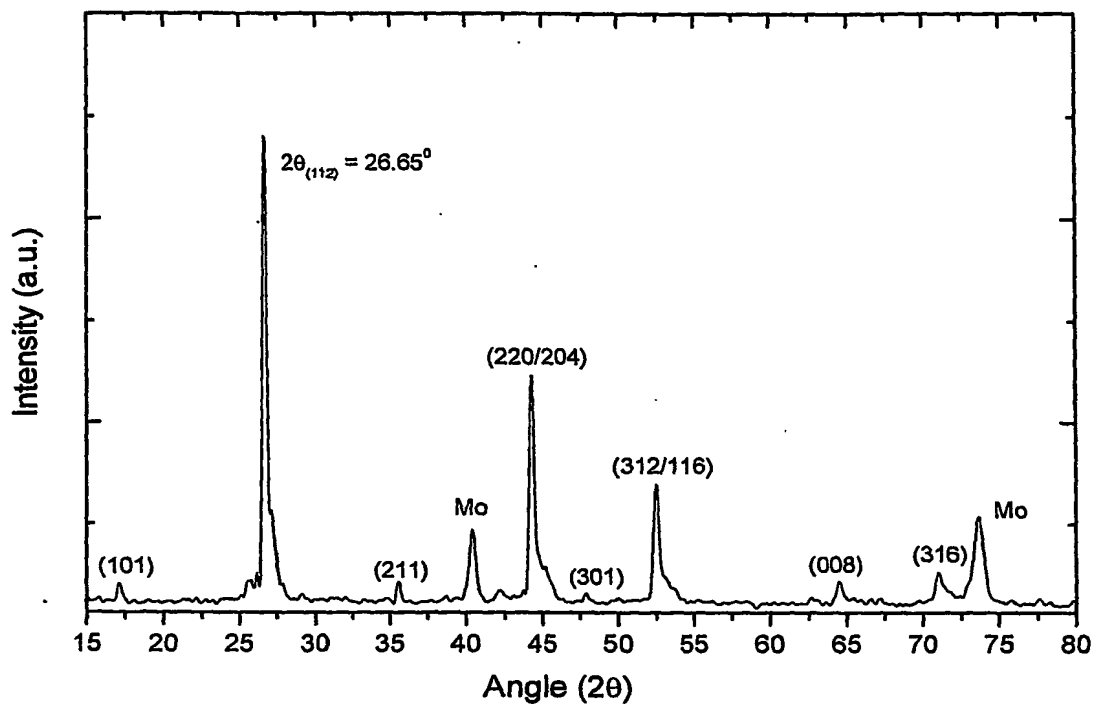


Figure 5.2

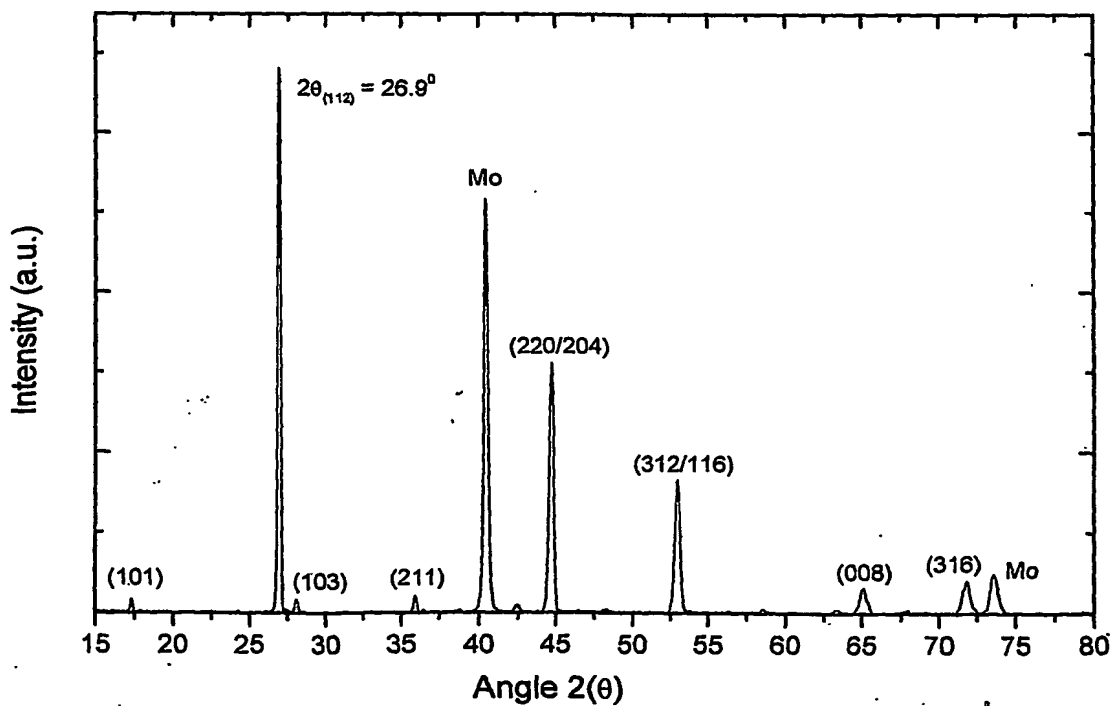


Figure 6.

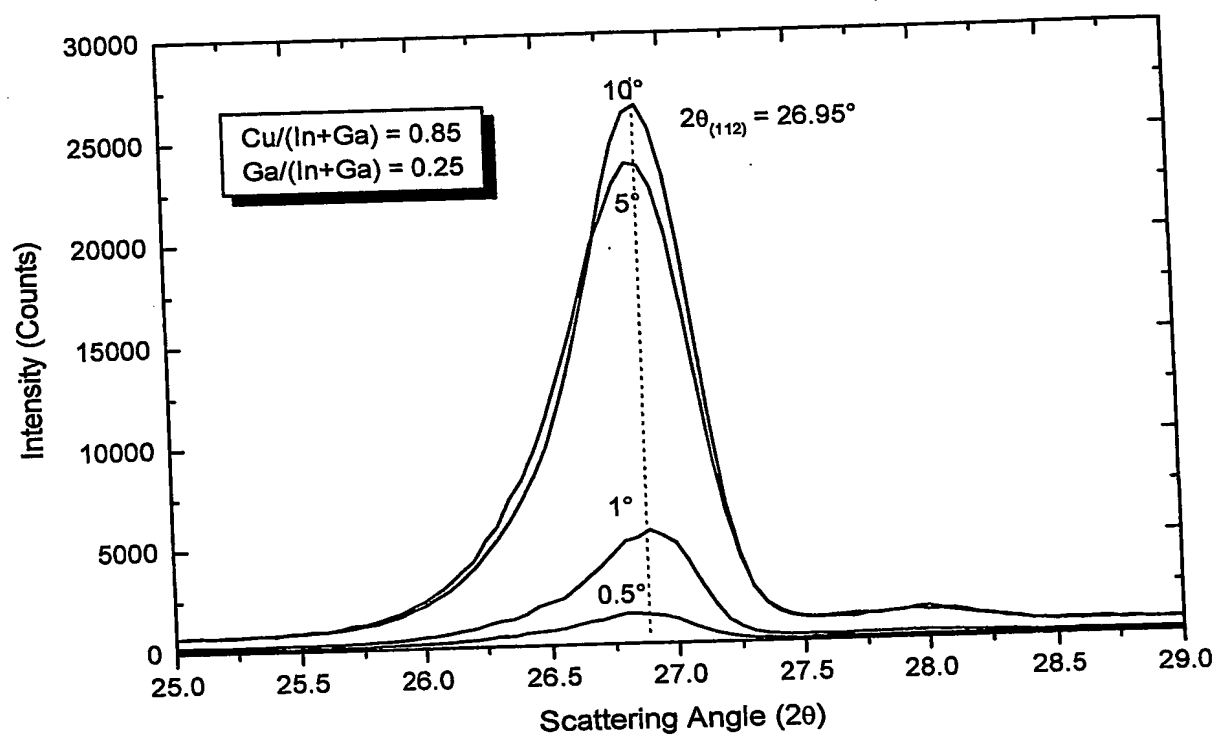


Figure 7.1.

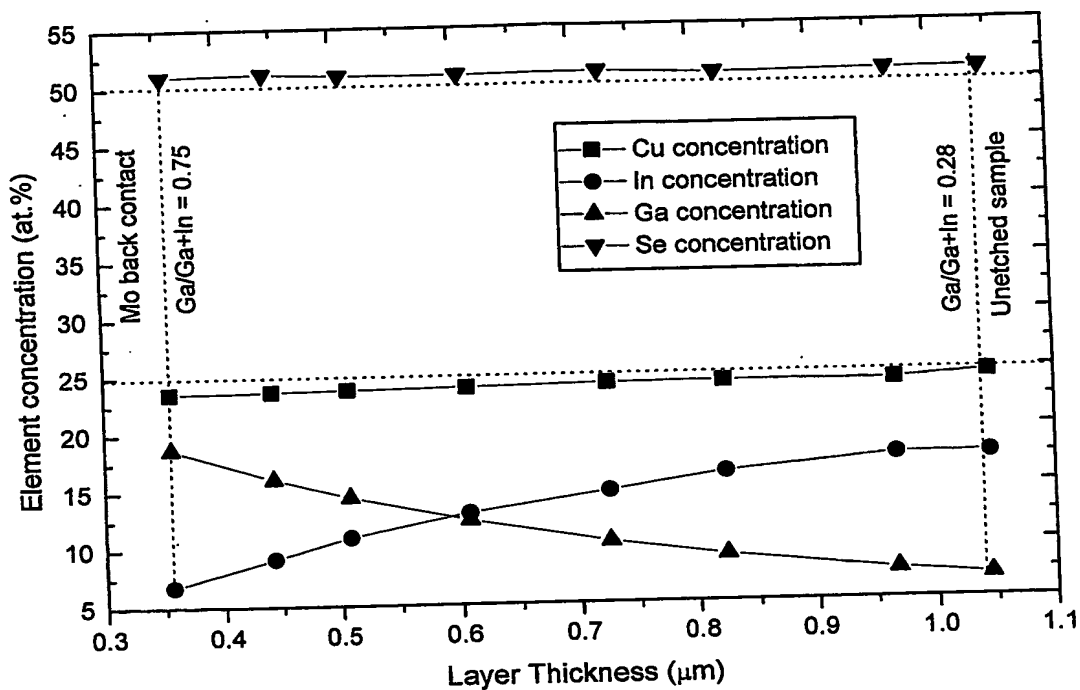


Figure 7.2.

